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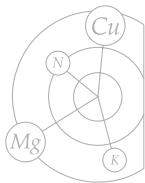
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HEAVY METALS IN THE UNSATURATED AND SATURATED ZONE OF THE UPPER JURASSIC CARBONATE MASSIF IN THE VICINITY OF KRAKÓW

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Abstract

Migration and concentration of heavy metals in infiltration waters within unsaturated and saturated zones of a carbonate massif result from their mobility as well as anthropopression. The purpose of this project, carried out in 1995-2005, was to observe changes in the chemical composition of infiltration waters, especially Sr, Ba, Fe, Mn, and Zn concentration in precipitations, in soils and in caves within an unsaturated zone and a saturated zone situated in a carbonate massif. Field research was conducted in the Prądnik River's drainage basin and at the Zakrzówek horst in Kraków. The chemical and mineralogical composition of limestone samples from 11 different quarries and natural exposures in the Kraków Upland were studied. The mineralogical research was conducted using the Roentgen diffraction method. The concentration of Sr, Ba, Fe, Mn and Zn in 700 samples from precipitation, caves and saturated zone waters was analysed. The determinations were made using mainly the ICP-AES Plasma 40 and ICP-MS Elan method. To assess the quality aspects of the migration of heavy metals, the results of the geochemical modelling were accounted for using the PHREEQC software. The hydrochemical research has shown distinct variability of concentrations of the analysed minor elements in different forms of precipitation (the highest concentrations being observed in sleet and the lowest in pure snowfall). In rainwater as well as in waters of the unsaturated and saturated zones, quantities of the five chemical elements appeared in the following decreasing order: Fe>Zn>Mn>Sr>Ba and Sr>Ba>Fe>Zn>Mn. The chemical composition of infiltration waters in the carbonate massif changes vertically. The fundamental trends in the waters of this area include an increase of Sr and Ba concentrations, a decrease of the concentration of Zn, and static concentrations of Fe and Mn.

Key words: water pollution, mobility of minor elements, karst environment, Kraków Upland.

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INTRODUCTION

Mechanisms involved in the migration of heavy metals through soils and other environmental matrices have long been of great interest to both environmental and soil scientists because of the risk of groundwater pollution by percolating heavy metals (DAM et al. 2008, ANGUELOV, ANGUELOVA 2009). In general, many types of soil or media contain a wide range of metals (including heavy ones), which occur in various concentrations depending on the surrounding geochemical conditions or anthropogenic sources (GLINA, BOGACZ 2013). Human activity clearly affects the metal content in soils, both at present and in the past (MASKALL et al. 1995, KANMANI, GANDHIMATHI 2013). Nowadays, the problems of sorption, adsorption and particularly migration of heavy metals are very important and have already been studied on various soil environments (DUBE et al. 2001, DOMAŃSKA 2009, KOWALKOWSKI, BUSZEWSKI 2002).

Karst limestone massifs constitute over 30% of the European Union's territory. Most are highly vulnerable to pollution, which is limited by the existence of epikarst features but elevated by swallow holes, into which surface streams sink. The degree of vulnerability to pollution is connected to the conservative and active types of pollutants such as chlorides and nitrates, respectively (FOSTER et al. 2013). Heavy metals, on the other hand, demonstrate varying degrees of environmental mobility (which is usually low) and high variability of concentrations in waters seeping through carbonate massifs, depending on natural as well as anthropogenic factors (NI et al. 2009, WITCZAK et al. 2013). According to FAIRCHILD et al. (2000) and ORLAND et al. (2014), concentrations of Mg and Sr in the groundwater of a saturated zone increases relative to Ca in drier conditions. This is because of prolonged groundwater-bedrock interaction, which adds higher proportions of Sr and Mg to the groundwater. On the other hand, enhanced degassing and calcite precipitation preferentially remove Ca from groundwater.

The purpose of this paper is to present directions of the evolution of the chemical composition of infiltration water, especially with the variability of the Sr, Ba, Fe, Mn, Zn concentrations in precipitation, soil, limestone and cave waters of the unsaturated zone, as well as in waters of the saturated zone in the Upper Jurassic carbonate massif located in the Kraków region.

MATERIAL AND METHODS

Study area

The research presented herein was conducted between 1995 and 2006 within the unsaturated and saturated zones of the Prądnik river catchment (in Ojców National Park; ONP). Additionally, between 1996 and 1997,

investigations covered the unsaturated zone of the Zakrzówek horst within the limits of Kraków (RÓŻKOWSKI 2006, MOTYKA, RÓŻKOWSKI 2003). The area of Ojców National Park and the Zakrzówek horst is built of the Upper Jurassic limestones and marls of the thickness between 150 and 220 meters (Figure 1). In some places, Cretaceous sandy and carbonate sediments, Paleogene saprolites, Miocene argils and loesses up to several meters thick occur as an overburden layer.

In the Zakrzówek horst area, according to the WRB soil classification system (2006), the following types of soils predominate: *Haplic Cambisol* (O-A-Bw-Ck), *Stagnic Cambisol* (O-A-Bwg-C), *Rendzic Leptosol* (A-AC-R), and *Cambic Leptosol* (Calcaric) of the O-A-Bw(ca)-Cca) profile type. The ONP area is dominated by *Haplic Luvisol* (O-A-Eet-Bt-C) soil, particularly ubiquitous on hilltops. The limestone parent rocks are covered by proper rendzina (Ol-A-Abbr-BbrCca-Rca) and typical brown rendzina (Ol-Aa-Abbr-Cg(ca)). Brown soil in this area is characterised by the acid reaction of pH 4.6-4.8 in water and 3.8-4.3 in KCl. The average concentrations of Fe, Mn and Zn in the humus horizon are 6480, 13 910 and 70 (mg kg⁻¹), respectively. The average Fe content in the B and C horizons reaches 10 400 and 19 040 mg kg⁻¹, respectively, while Zn equals 45 and 61 mg kg⁻¹ (ZALEWA 2008).

The Upper Jurassic aquifer of the Kraków Upland covers a heterogeneous, discontinuous and anisotropic carbonate massif, which constitutes a triple porosity medium. Recharge of the aquifer, mainly of the dispersed

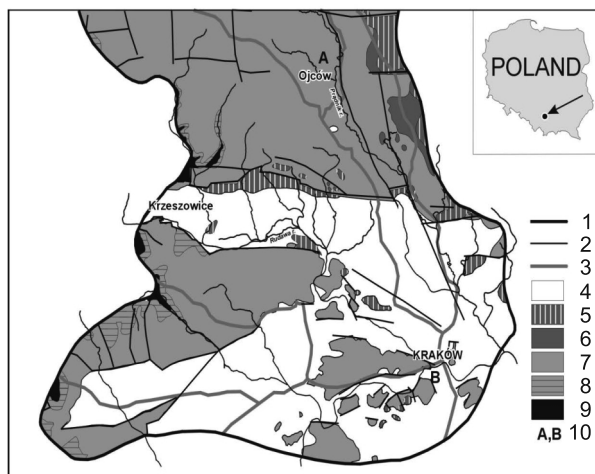


Fig. 1. Geological map of the Kraków Jurassic massif (without Quaternary sediments, according to JÓZWIĄK, KOWALCZEWSKA, 1984):

1 - limits of the Upper Jurassic aquifer; 2 - main faults; 3 - roads; sediments: 4 - Neogene: clays, claystones, siltstones, sands, sandstones, gypsum, 5 - Upper Cretaceous: marls, limestones, 6 - Lower Cretaceous: sands, sandstones, conglomerates, 7 - Upper Jurassic: limestones, marls, 8 - Middle Jurassic: clays, mudstones, conglomerates, marls, limestones, 9 - Carboniferous and Devonian: claystones, siltstones, sandstones, hard coal, limestones, marls, dolomites, 10 - study area: A - Prądnik river catchment, B - Zakrzówek horst

type, occurs over the entire outcrop area and also indirectly through the overlying Quaternary deposits. The considerable thickness (up to 100 m) of the unsaturated zone and a relatively thin saturated zone (up to 150 m) result from the deep cut of the karstic aquifer (RÓŻKOWSKI 2006).

The area under study is remarkable for the high vulnerability of the Upper Jurassic aquifer to pollution. The hazard is due to the lack or a small thickness of the soil cover. The soil has little protective capacity. The approximate time of water replacement in 1 meter of the soil profile is no more than 1.7 year, being as short as 0.2 year in the limestones of the unsaturated zone. The lateral migration of conservative substances in the fissure-karstic aquifer is very rapid, reaching over 300 meters per year (WITCZAK et al. 2011). Tracer experiments using Cl ion revealed that the transport velocity through the unsaturated zone of Zakrzówek ranges from 146 to 1533 m/a (MOTYKA et al. 2002). The water residence time in the Upper Jurassic aquifer of the Rudawa catchment (located south of the Prądnik catchment), determined on the basis of the natural concentrations of tritium ranges from 65 to 130 years, while in the fissure-karstic systems it does not exceed 6 years (RÓŻKOWSKI 2006).

Mineralogical analysis

During our investigation on the chemical and mineralogical composition of the limestones, samples from 11 quarries across the Kraków Upland were collected. Mineralogical studies were performed in the X-ray Diffraction Laboratory of the University of Silesia. Powdered samples were analysed using an X-ray diffractometer model Panalytical X'Pert PROMPDPW3040/60, and applying Co K_{α1} radiation with an Fe filter and X' Celerator detector. Quantitative and qualitative studies were carried out using the computer program X'Pert HighScorePlus, as well as the patterns database ICDDPDF-4 and structural patterns database ICSD.

Hydrochemical analysis

The chemical analyses of 700 samples of rainwater, infiltrating water from the unsaturated zone and groundwater sampled from the saturated zone were carried out in the laboratories of the University of Silesia and the University of Science and Technology in Kraków, using an ICP-AES Plasma 40 by Perkin-Elmer and ICP-MS Elan 6100. To assess the qualitative aspects of the migration of heavy metals, the results of the geochemical modelling (conducted using the PHREEQC software) were taken into account (RÓŻKOWSKI 2005, 2006, RÓŻKOWSKI et al. 2005, MOTYKA, RÓŻKOWSKI 2003, MOTYKA et al. 2005).

The chemical evolution of water in the unsaturated zone of limestones was investigated in detail at the Zakrzówek horst, within the karst system impacted by the anthropogenic processes of the urbanised area of the city of

Kraków. The hydrochemical research consisted of 70 analyses of precipitation water and 421 analyses of percolating water from seven caves (MOTYKA, RÓŻKOWSKI 2003, MOTYKA et al. 2005).

RESULTS AND DISCUSSION

Concentrations of minor elements in the soils of the Kraków Upland vary significantly, as documented by LIS and PIASECZNA (2001). On average, they are as follows (in mg kg^{-1}): Sr: 10-20 (max. 160); Ba: 5-50 (maximum 100); Fe: 5000-10 000 (max 20 000), Mn 250-500 (max.1000), Zn 70-200 (max. 500). The upper limits of the geochemical background of the before mentioned elements estimated for entire Poland are: Sr 30, Ba 750, Fe 19 000, Mn 2000 and Zn 300 mg kg^{-1} (LIS, PIASECZNA 2001, WYSZKOWSKA, WYSZKOWSKI 2002).

MASCALL et al. (1995) identified the (pH) reaction of the soil as the principal mechanism controlling the vertical migration of Pb and Zn. These authors also showed that low metal mobility is related to an increase of pH in soils owing to the release of calcium from carbonate. The low pH increases the mobility of metals in soil and their availability to organisms (SELIM, SPARKS 2001, MARKO-WORŁOWSKA, CHRZAN 2010). The soils studied had alkaline reaction (from 7.3 to 7.7), which does not promote the mobility of metals in the vertical profile. The rate of migration as well as concentrations of heavy metals in different soil systems and ecosystems are strictly related to the sources of heavy metals, which are often of anthropogenic origin. An important role is played by the chemical composition of the exposed materials (BENCHEA et al. 2011, GLINA, BOGACZ 2013).

The geochemical studies have shown that the content of minor elements in limestones of the Kraków Upland varies: between 184 and 1185 for Fe, 87 to 211 for Mn, from 64 up to 129 for Sr and 10 and 76 for Zn (all in mg kg^{-1}), reaching relatively: Fe $1.84 \cdot 10^{-2}$ -0.12, Mn $8.75 \cdot 10^{-3}$ - $2.11 \cdot 10^{-2}$, Sr $6.40 \cdot 10^{-3}$ - $1.29 \cdot 10^{-2}$, Zn $1.04 \cdot 10^{-3}$ - $7.63 \cdot 10^{-2}$ (%). Low magnesium calcite is the main component, while the secondary ones include quartz, clay minerals and, sporadically, Na-feldspars (sanidine) and Ca-feldspars (albite), volcanic glass, goethite-hematite and pyrite (RÓŻKOWSKI 2006). Similar studies conducted on limestones of the Zakrzówek horst revealed variable concentrations of Fe 500-1700, Mn 120-1300, Sr 108-126 and Zn 18-60 (mg kg^{-1}).

The chemical composition of groundwater within the Kraków Upland's area changes in the vertical profile (Figure 2). The quantitative analysis of the hydrochemical transformation in the vertical profile of the partial catchment of the Prądnik River revealed that a radical modification of the chemical composition of the infiltrating water takes place in relation to the precipitation, as a result of intensive leaching of the soil matrix and ion exchange process. In the oxidizing, neutral or alkaline environment of the

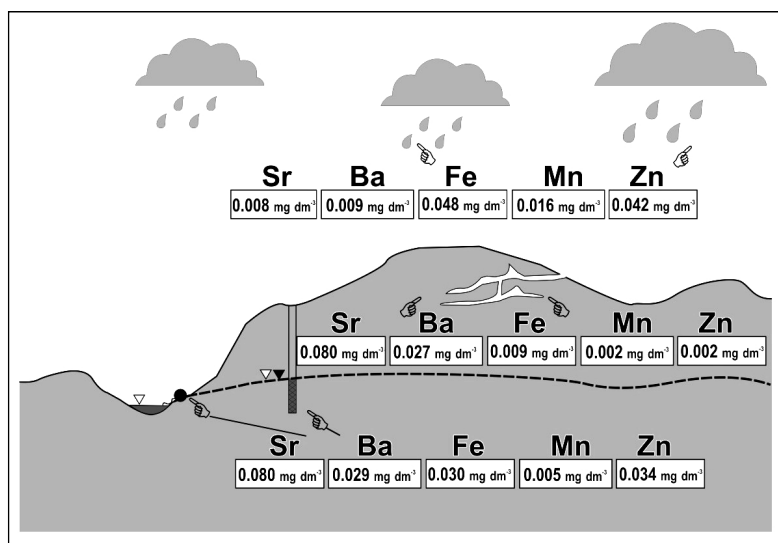


Fig. 2. Concentrations of minor elements in the hydrosphere of the Cracow Upland
Precipitation - mean concentrations acc. to Table 2; Unsaturated and saturated zone - values
acc. to Table 1

Kraków Upland's Upper Jurassic limestones, Sr is a highly mobile aquatic migrant (in the cation form), Ba and Zn are less mobile while Fe and Mn are immobile, static elements (WITCZAK et al. 2013). This is in agreement, *inter alia*, with the results of the research on a limestone hydrosome complex in the Netherlands (MENDIZABAL et al. 2011). At the same time, Zn belongs to mobile aquatic migrants, especially in the acidic environment (MAŁECKI, MATYJASIK 2000).

The average concentrations of minor elements in precipitation within the Prądnik River catchment reach: Sr 0.002, Ba 0.005, Fe 0.062, Mn 0.025, Zn 0.079 (mg dm⁻³). In the cave water of the unsaturated zone, the mean concentrations change to: Sr 0.080, Ba 0.027, Fe 0.009, Mn 0.0023, Zn 0.0023 (mg dm⁻³), while the median values obtained from the saturated zone reach: Sr 0.080, Ba 0.029, Fe 0.030, Mn 0.005, Zn 0.034 (mg dm⁻³).

Assuming the average precipitation of 0.00198 m d⁻¹, the volume of infiltration of 518 m³ d⁻¹ km⁻² and the total subsurface runoff of 524 m³ d⁻¹ km⁻² (derived from mathematical modelling, using the MODFLOW software), basic calculations were made to estimate loads of minor elements in the hydrosphere of the Prądnik catchment. The general formula $G = M \cdot c$ (kg d⁻¹ km⁻²) was used to calculate the load, where: G – load, M – coefficient (of MP – mean precipitation, M_v – precipitation infiltration, M_f – total subsurface runoff); c – mean concentration of a selected component in water (RÓŻKOWSKI 2006). The results are presented in Table 1. The median values of the same constituents in the waters of the saturated zone from the whole southern part of

Table 1

Mean concentrations and loads of the minor elements in the hydrosphere of the upper part of the Prądnik catchment (area of 98 km²)

Minor element	Precipitation $n = 70$		Unsaturated zone $n = 43$		Saturated zone $n = 100$	
	mean concentration (mg dm ⁻³)	load (kg d ⁻¹ km ⁻²)	mean concentration (mg dm ⁻³)	load (kg d ⁻¹ km ⁻²)	median concentration (mg dm ⁻³)	load (kg d ⁻¹ km ⁻²)
Sr	0.002*	0.003	0.080	0.041	0.079	0.041
Ba	0.005*	0.010	0.027*	0.014	0.029	0.015
Fe	0.062*	0.123	0.009	0.004	0.030	0.016
Mn	0.025*	0.050	0.002*	0.001	0.005	0.002
Zn	0.079*	0.156	0.002*	0.001	0.034	0.018

* data from the years 1996 to 1998 according to MOTYKA et al. (2002)

the upland differ slightly, reaching the following values: Sr 0.099, Ba 0.037, Fe 0.022, Mn 0.001, Zn 0.033 (mg dm⁻³). However, the variability interval is much more diversified: Sr 0.004-1.813, Ba 0.005-0.249, Fe 0.001-6.330, Mn 0.001-0.920, Zn 0.002-0.994 (mg dm⁻³). These ranges correspond to mean concentrations typical of natural groundwater: Sr 0.185, Ba 0.01-0.30, Fe 0.02-5.0, Mn 0.01-0.40, Zn 0.005-0.05 (mg dm⁻³) (WITCZAK et al. 2013).

In the precipitation collected in the Zakrzówek area, conductivity changes from 7 to 405 $\mu\text{S cm}^{-1}$ (with the modal value of 38 $\mu\text{S cm}^{-1}$). The mean pH changed, depending on the type of the precipitation, to 5.97 in rain, 5.48 in sleet and 4.93 in snow. The highest concentrations of minor elements were found in sleet, lower in rain and the lowest in snow (Table 2).

Minor elements enrich rainwater during weathering processes, combustion of fossil fuels and anthropogenic industrial emissions. Heavy metals, especially those which at temperatures typical of furnaces turn into the gaseous state (Cd, Zn, Pb, Hg), condense while forming a smoke cloud on dusty particles and then are carried together as suspension (DIBOFORI-ORJI, EDORI 2013). The low pH of water condensing in the atmosphere favours the ionic form of metals.

The pH reaction of the water from the unsaturated zone of the Zakrzówek horst varies from slightly acidic (6.82) to slightly alkaline (max. 8.62). The acidity of the infiltrating precipitation water radically decreases as a result of calcite and dolomite dissolution in the presence of CO₂. Conductivity of the water sampled in the cave system of the horst differs spatially from 130 to 2160 $\mu\text{S cm}^{-1}$.

The migration of metals within soil is strictly connected with the soil properties, both chemical and physical ones, which together determine the binding ability of the soil. Fe ions introduced to the system with meteoric water reach the soil, where they are absorbed by plants as a biophilic element. Fe ions form active geochemical compounds, such as oxides and

Table 2

Basic statistical parametres of concentrations of the selected minor element in the types of precipitation at the Zakrzówek area

Minor ele- ment	Type of precipitation	Popu- lation	Min.	Max.	Range	Arith- metic mean	Geo- metric mean	Median	Standard deviation
			(mg dm ⁻³)						
Fe	precipitation	70	0.005	0.593	0.588	0.048	0.027	0.033	0.074
	rain	42	0.005	0.133	0.128	0.037	0.023	0.030	0.034
	snow	21	0.005	0.593	0.588	0.061	0.027	0.039	0.124
	sleet	7	0.023	0.150	0.127	0.073	0.060	0.078	0.043
Mn	precipitation	70	0.001	0.091	0.090	0.016	0.010	0.010	0.016
	rain	42	0.001	0.053	0.052	0.015	0.010	0.010	0.013
	snow	21	0.001	0.057	0.056	0.013	0.009	0.008	0.013
	sleet	7	0.001	0.091	0.090	0.030	0.013	0.019	0.031
Zn	precipitation	70	0.001	0.168	0.167	0.041	0.024	0.029	0.038
	rain	42	0.001	0.168	0.167	0.028	0.015	0.018	0.032
	snow	21	0.013	0.127	0.114	0.056	0.046	0.047	0.035
	sleet	7	0.005	0.143	0.138	0.073	0.048	0.076	0.049
Sr	precipitation	70	0.000	0.041	0.040	0.008	0.004	0.005	0.008
	rain	42	0.000	0.041	0.040	0.008	0.005	0.006	0.008
	snow	21	0.001	0.029	0.028	0.007	0.003	0.003	0.008
	sleet	7	0.001	0.017	0.016	0.009	0.005	0.010	0.007
Ba	precipitation	70	0.001	0.031	0.030	0.009	0.005	0.006	0.008
	rain	42	0.001	0.030	0.029	0.009	0.005	0.009	0.007
	snow	21	0.001	0.031	0.030	0.009	0.005	0.004	0.009
	sleet	7	0.001	0.012	0.011	0.006	0.004	0.006	0.004

hydroxides, as well as complexes with organic substances. Fine-grained and colloidal hydroxides are largely subject to sorption on the surface of mineral grains and organic particles. Fe ions migrating in shallow groundwater undergo multiple processes of precipitation and remobilisation, depending on the changing reaction and Eh conditions (WITCZAK et al. 2013). In the entirely carbonate environment of the Zakrzówek horst, where demobilisation processes prevail, Fe ions decrease their presence in the water to 0.01 mg dm⁻³. The tendency for quick precipitation of Fe compounds in oxidising and alkaline environment is confirmed by the saturation indices calculated with PHREEQC software (Table 3). Mn and Zn ions behave similarly. The Mn content is mostly limited by the solubility of manganese carbonates. The compounds dissolved in water precipitate rapidly, usually in the form of

Table 3

Saturation indices (SI)* for selected mineral phases in relation to the water in precipitation and in four caves of the Zakrzówek horst

Precipitation	Barite	Celestite	Strontianite	Goethite	Hematite	Fe(OH) ₃
	-1.58	-5.19	-6.76	+2.44	+6.81	-2.58
Caves	from -1.09 to -0.24	from -1.09 to -0.24	from -3.72 to -2.89	from +6.74 to +8.71	from +15.41 to +19.35	from +1.49 to +3.46

* For the calculation of SI values, selected representative chemical analysis were chosen (similar to the average values in individual subpopulations) for rainfall and four different cave systems

oxides and hydroxides. The Mn ion also forms complex compounds. Zn ions in soils containing clay minerals are subjected to strong sorption. At higher acidity, Zn is also absorbed by organic matter (BADORA 2002).

In soils formed on limestone bedrock, Sr undergoes leaching and is substituted by other divalent cations in ion exchange processes. By being similar to a Ca ion and therefore occurring in calcite crystal structures, Sr is released during limestone dissolution, in amounts dependent on the mineralogical composition and solubility indexes of the primary minerals. Ba is distinguished by its ion's radius larger than that of Ca, making its incorporation into calcite structures difficult. During the weathering, Ba easily transforms into solutions, especially in the soil environment, and precipitates in the form of hardly dissoluble carbonates and sulphates. With similar concentration of Sr and Ba in meteoric waters (mean value of 0.006 mg dm⁻³), in exudations sampled in the cave systems, significant enrichment of the Sr concentration was discovered, up to the mean value of 0.0580 mg dm⁻³, with just a small rise of the Ba concentration, up to the value of 0.016 mg dm⁻³ (Table 4).

Table 4

Basic statistical parametres of the minor elements in waters of the unsaturated zone of the Zakrzówek horst

Minor element	Population	Min.	Max.	Range	Arithmetic mean	Geometric mean	Median	Standard deviation
(mg dm ⁻³)								
Fe	424	0.001	4.319	4.318	0.064	0.012	0.005	0.285
Mn	425	0.000	0.044	0.044	0.003	0.002	0.001	0.005
Zn	425	0.001	0.313	0.312	0.006	0.002	0.001	0.021
Sr	424	0.001	0.585	0.584	0.070	0.059	0.058	0.049
Ba	424	0.001	0.092	0.091	0.018	0.013	0.016	0.013

CONCLUSIONS

1. In the urban area of Kraków, concentrations of minor elements in precipitation in 1996-1997 were highly divergent (Fe 0.005 - 0.593, Mn 0.001 - 0.091, Zn 0.001 - 0.168, Sr 0.0005 - 0.041, Ba 0.001- 0.031 mg dm⁻³). The low reaction of precipitation (mean pH of rainfall 5.97, sleet 5.48, snow 4.93) favours the ionic form of metal. In the selected groups of precipitation, various concentrations of ions were determined (the highest concentrations were observed in sleet while the lowest ones were in snow). Higher concentrations were recorded for Fe, Mn and Zn (median values: Fe 0.033, Mn 0.0108, Zn 0.029), while lower ones for Sr and Ba (median values Sr 0.0056, Ba 0.006 mg dm⁻³).

2. Migration of heavy metals in a soil profile is strictly related to the environment's properties, both chemical and physical ones, which together determine the binding ability of soil. On the other hand, mobility of heavy metals in soil is also determined by the particle size distribution as well as the content of clay and other fine fractions. The share of clayey material and the base saturation at the bottom of the profile impede migration of minor elements into the depth of a rock mass.

3. Chemical composition of the infiltrating water in the carbonate massif of the Kraków Upland evolves in the vertical profile. Concentrations of Sr and Ba increase. In the carbonate environment, with the predominating demobilisation processes, Fe, Mn, and Zn decrease their presence in the water.

4. The detailed studies conducted at the Zakrzówek horst showed that the concentrations of the observed minor elements in the cave waters vary significantly: Fe 0.001-4.319, Mn 0-0.044, Zn 0.001-0.313, Sr 0.001-0.585; Ba 0.001-0.092 (mg dm⁻³). The large variability of the results from the complex circulation conditions in the fracture-karst-porous carbonate massif and from locally strong anthropogenic impact.

5. Below the epikarst zone and the upper part of the unsaturated zone, the process of limestone dissolution by percolating water has moderate dynamics. The average concentrations of minor elements in the waters sampled from the caves of the unsaturated zone explored within the karstic catchment of the Prądnik River reached the following values: Sr 0.080, Ba 0.027, Fe 0.009, Mn 0.0023, Zn 0.0023 (mg dm⁻³). Median values in the waters sampled from the saturated zone changed to: Sr 0.080, Ba 0.029, Fe 0.030, Mn 0.005, Zn 0.034 (mg dm⁻³).

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